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Strategies of engineering 2D nanomaterial-based electrocatalysts toward hydrogen evolution reaction

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Abstract

© 2020, The Author(s). Electrochemical water splitting driven by renewable energy-derived electricity is considered as the most promising pathway for delivering clean and sustainable hydrogen production. The key to achieving an efficient water splitting process is developing highly active electrocatalysts. Two-dimensional (2D) nanomaterials hold great promise in the electrocatalysis field due to their unique physicochemical properties. Some of them are not active enough because of the poor intrinsic activity, low density of active sites or low electrical conductivity. Some are inert for electrocatalytic reactions, but are able to work as the functional substrates for hybrid electrocatalysts. Thus, tremendous strategies have been developed to modulate the physicochemical and electronic properties of 2D nanomaterial-based electrocatalysts, and to make full use of the functionalities of functional 2D nanomaterial substrates to achieve fast catalytic reaction kinetics. In this review, the recent progress on the well-established design strategies for the 2D nanomaterials-based electrocatalysts is highlighted. The perspectives on the current challenges and future development of 2D electrocatalysts are addressed.

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REVIEW PAPER

Strategies of engineering 2D nanomaterial-based electrocatalysts toward hydrogen evolution reaction

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Abstract

Electrochemical water splitting driven by renewable energy-derived electricity is considered as the most promising pathway for delivering clean and sustainable hydrogen production. The key to achieving an efficient water splitting process is developing highly active electrocatalysts. Two-dimensional (2D) nanomaterials hold great promise in the electrocatalysis field due to their unique physicochemical properties. Some of them are not active enough because of the poor intrinsic activity, low density of active sites or low electrical conductivity. Some are inert for electrocatalytic reactions, but are able to work as the functional substrates for hybrid electrocatalysts. Thus, tremendous strategies have been developed to modulate the physicochemical and electronic properties of 2D nanomaterial-based electrocatalysts, and to make full use of the functionalities of functional 2D nanomaterial substrates to achieve fast catalytic reaction kinetics. In this review, the recent progress on the well-established design strategies for the 2D nanomaterials-based electrocatalysts is highlighted. The perspectives on the current challenges and future development of 2D electrocatalysts are addressed.

Keywords 2D nanomaterial · Electrocatalysts · Hydrogen evolution reaction · Electrochemical water splitting

Introduction

The energy shortage and environmental issues caused by the overuse of insufficient fossil fuels are becoming two urgent challenges for current society [1, 2]. Exploiting the clean and renewable energy sources (e.g., wind, solar, etc.) is highly desirable to meet the long-term energy demand and environmental sustainability. However, the utilization efficiencies of renewable energies are always limited by their unpredictability and discontinuity. Thus, to make efficient use of renewable energy, developing advanced energy storage and conversion technologies is of great significance. Among the energy conversion technologies, one of the most attractive and promising options is renewable energy electricity-driven water splitting for hydrogen generation, which includes two electrochemical processes of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [3, 4]. The key to the promotion of the water-splitting kinetics is to design highly active HER and OER electrocatalysts. To date, precious metal-based catalysts like Ir, Pt, and RuO_2 are extensively employed for the two reactions. However, they suffer from high-cost, low-scarcity, and insufficient stability, which would severely limit their large-scale applications [5–10]. Therefore, seeking for cost-effective alternatives with high catalytic performance to noble metal-based electrocatalysts is greatly important for the development and substantial commercialization of economic water splitting technologies.

Since 2D graphene was discovered, numerous 2D nanomaterials have aroused plenty of research interest in the fields of energy conversion and storage [11, 12]. In particular, 2D nanomaterials have become one of the most promising candidate materials for the design and development of electrocatalysts due to their unique physic chemical properties and electronic structures [13–16]. However, some 2D nanomaterials are not active enough because of the poor intrinsic activity, low density of active sites or weak conductivity. Some 2D nanomaterials are inert for electrocatalysis, but can act as functional substrates to boost the catalytic activity of hybrid electrocatalysts. Thus, numerous strategies

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have been developed to modulate the physicochemical and electronic properties of 2D material-based electrocatalysts, and to make full use of the functionalities of functional 2D nanomaterial substrates to achieve fast catalytic reaction kinetics [17–23].

In this review, we summarized the design and construction strategies for 2D nanomaterial-based HER electrocatalysts. These strategies are categorized into five types, including heteroatom doping, defect engineering, interface engineering, phase engineering, and geometric engineering. The underlying mechanisms for enhancing the catalytic activity are also discussed. Finally, the challenges and perspectives for 2D material-based HER electrocatalysts are proposed.

Engineering protocols for 2D electrocatalysts

2D nanomaterials have been extensively applied in the electrocatalysts due to their adjustable and evenly exposed lattice planes, unique physicochemical properties, and electronic structures. These special features can have remarkable influences on the extrinsic and intrinsic activities of electrocatalysts. Apart from the adjustable catalytic activities, 2D nanomaterials can also work as functional supports because of their large specific surface areas and robustness for the development of hybrid electrocatalysts. However, most pure 2D electrocatalysts are inert or not active enough because of the poor intrinsic activity, low density of active sites, and low electrical conductivity [24–26]. Thus, some efficient optimization strategies (including heteroatom doping, surface/interface building, defect constructing, geometric controlling, etc.) are already proposed for 2D electrocatalysts to achieve higher catalytic activities. These optimization approaches aim to modulate the surface/interface properties and electronic structures correlated with hydrogen adsorption free energy and charge/mass transfer kinetics, which would affect catalytic kinetics. In this section, a variety of design strategies for 2D nanomaterial-based electrocatalysts are summarized and some typical demonstrations are highlighted.

Heteroatom doping

Heteroatom doping is considered as an efficient approach to modulating the electronic states, controlling the surface/interface properties, and altering the elementary compositions of 2D electrocatalysts. So far, heteroatom doping method for 2D nanomaterials is mainly applied in the cases of layered double hydroxides (LDHs), graphene, transition-metal dichalcogenides (TMDs), g-C_3N_4, etc. Both non-metal atoms and metal atoms have been extensively studied as the dopants. Doping graphene with one or more non-metal heteroatoms is the most efficient way for boosting electrocatalytic performance of graphene-based catalysts [27]. Among the single-heteroatom-doped graphene nanomaterials, N-doped graphene-based catalysts are the pioneer of non-metal-atom doped 2D electrocatalysts. N atom is the most common and efficient dopant for carbonaceous materials. Since the size and electronegativity of N atoms are different from those of C atoms, the electronic states of carbonaceous catalysts could be modulated by N doping via the conjugation effects between nitrogen lone electronic pairs and carbon π-system [28, 29]. B-doped graphene exhibits exceptional HER performance [30], but the activity is still inferior to those of the MoS_2-based and Pt-based electrocatalysts. Moreover, DFT calculations found that although doping heteroatoms in graphene can enhance the hydrogen adsorption ability, all the ΔG_{H^*} values are still positive, demonstrating unfavorable thermodynamic adsorption process. Thus, all heteroatom-doped graphene catalysts locate at the right branch bottom in the volcano curves (Fig. 1a) [30]. To rank the catalytic activity of graphene-based electrocatalysts in volcano plots, a basic principle of optimizing ΔG_{H^*} was proposed by Qiao et al. according to the Hückel molecular orbital theory (HMOT). The results showed that the higher the density of state (DOS) position, the better the linearity between the DOS and the ΔG_{H^*}, which also indicates the stronger hydrogen adsorption strength (Fig. 1b). In addition, they demonstrated that the position of the DOS closer to the Fermi level shows stronger interaction with the adsorbed hydrogen intermediates, accordingly achieving a lower ΔG_{H^*} value. Motivated by the findings, N, P, S, Br, and O heteroatoms were investigated as the dopants. These heteroatoms commonly substitute or disrupt the carbon atoms at the edge areas and basal planes to form more defect sites, which can work as the active sites, facilitating the eletrocatalytic processes [31, 32]. As is well known, the catalytic activity is dominated by the density of the exposed active sites and the intrinsic activity of active centers that are correlated with the extrinsic geometric characteristics. For the doped graphene-based catalysts, the total exposure number of active sites is closely connected with the doping levels and specific surface area. Thus, in addition to the selection of doped heteroatoms, the doping degree and specific surface area should also be taken into account for enhancing HER activities of graphene-based catalysts.

In addition to heteroatom-doped 2D carbon-based electrocatalysts as discussed in the previous sections, doping 2D TMD-based electrocatalysts with heteroatoms can also modulate the catalytic activities. Heteroatom doping can efficiently create additional active sites and tune the electronic states of TMDs, directly enhancing the extrinsic and intrinsic activity [33–35]. Our group investigated Ni/Co-doped $MoSe_2$ nanosheets as an effective alkaline HER

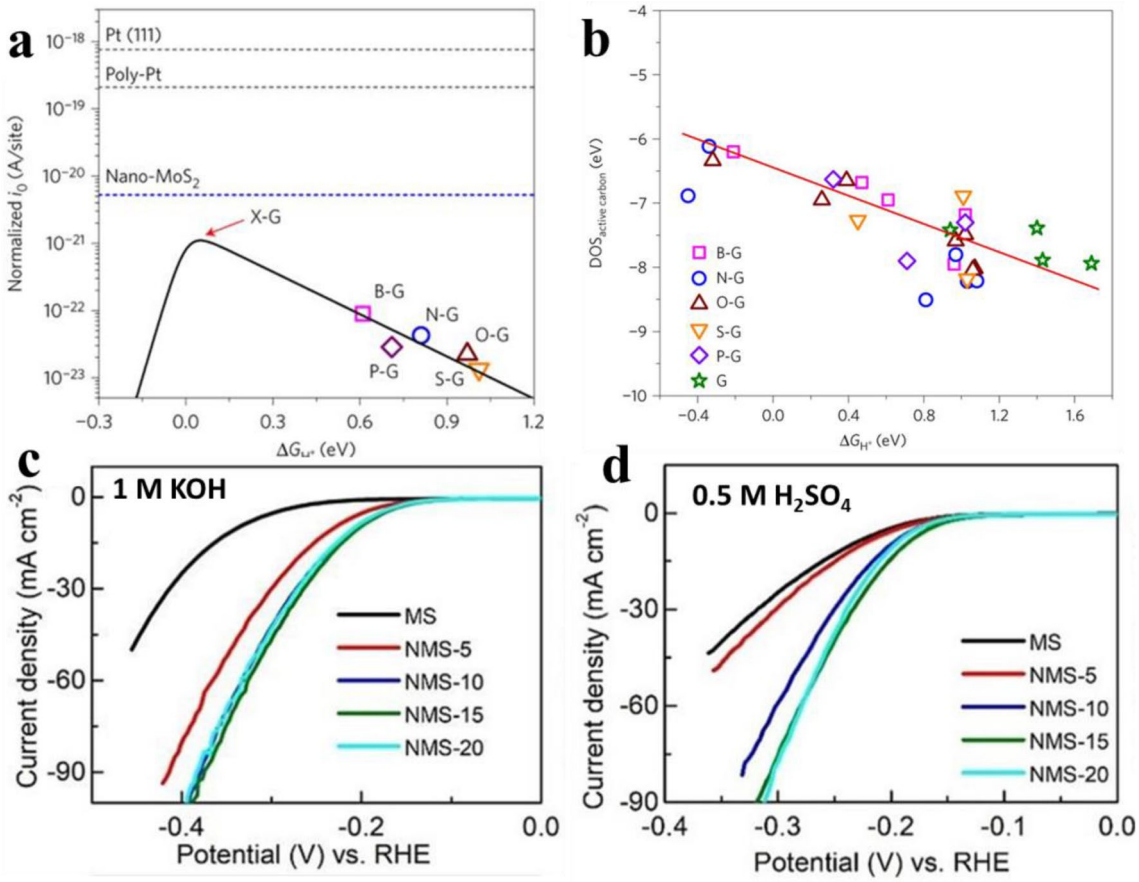

Fig. 1 **a** HER volcano plots containing $i_{0/site}{}^{theory}$ (solid black curve) and $i_{0/site}{}^{experiment}$ obtained from Tafel plots (colored open symbols) versus ΔG_H^* for each graphene model. The blue and gray dashed lines from nano-MoS_2 and single-crystal and polycrystalline Pt as the targets for optimization. **b** The relationship between ΔG_H^* and the highest peak position of DOS of the graphene-based materials; the red line is a guide for the eye [30], **c**, **d** LSV curves of the $MoSe_2$ and Ni-doped $MoSe_2$ catalysts in alkaline and acidic media, respectively [36]

electrocatalysts [36]. Ni- or Co-doped $MoSe_2$ catalysts deliver a slight promotion of acidic HER performance, but a substantial enhancement of HER activity in alkaline media as compared with bare $MoSe_2$ (Fig. 1c, d). Experimental results and DFT calculations demonstrate that Ni or Co doping, in addition to boosting the ability of water adsorption, optimizes the hydrogen adsorption free energy (ΔG_H) on the basal plane of $MoSe_2$ nanosheets. Besides, doping Fe, Co, or Ni etc. could also activate inert basal planes, such as the activation of in-plane S sites, which can greatly increase the amount of active sites [37–39].

Defect engineering

Engineering defects (nano nano-holes, vacancies, etc.) is an efficient way to modulate the electronic structures and physicochemical properties of 2D nanomaterial-based electrocatalysts, which can strongly affect their extrinsic and intrinsic activities [40–43]. Some reports claimed that the catalytic activity of MoS_2 originates from the edge Mo sites [44, 45]. Introducing S vacancies into the basal planes can not only modify the band gaps but also create additional exposed Mo edge sites [44, 46, 47]. Xie's group utilized a large-scale approach to introducing defects on the surface of MoS_2 to generate more active edges [48]. The HRTEM results confirm the formation of disordered atomic arrays on the basal planes, which can cause the crack of the basal planes, generating more additional edges (Fig. 2a–c). Ajayan's group constructed abundant defects within the monolayer of MoS_2 via hydrogen treatment and oxygen plasma exposure [49]. The formation of these defects significantly increases the total number of the exposed active edge sites, significantly enhancing HER kinetics (Fig. 2d–g). Moreover, the constructed defects can cause the lattice strains, which also modulate the band gaps of 2D materials. Li et al. introduced S vacancies and strains in the monolayer 2H-MoS_2 basal plane for improved HER activity [50]. The S vacancies with band states approaching the Fermi level can

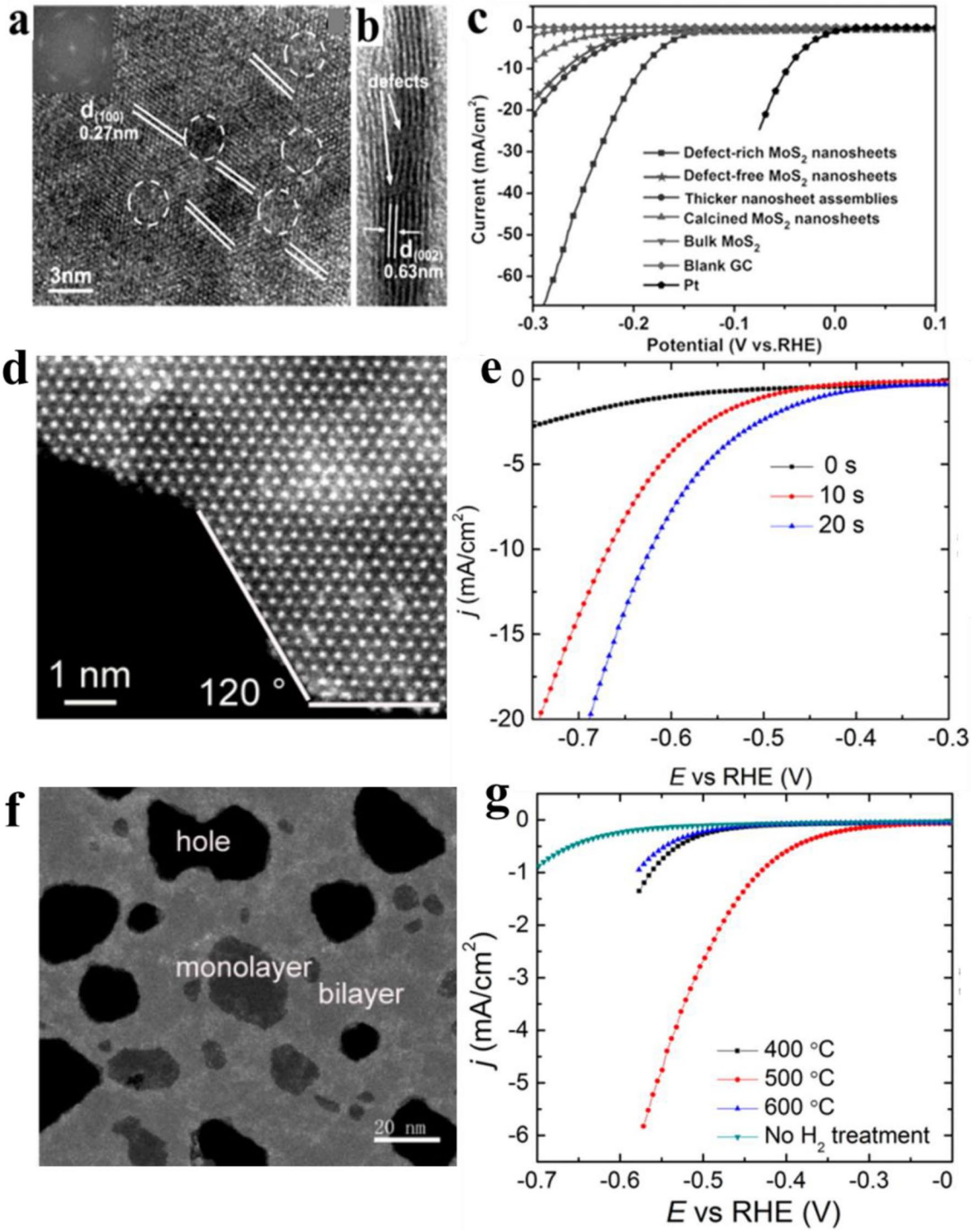

Fig. 2 **a** HRTEM image and the corresponding FFT patterns of the defect-rich MoS_2 ultrathin nanosheets. **b** Cross-sectional HRTEM image of the defect-rich MoS_2 ultrathin nanosheets. **c** Polarization curves of the defect-free MoS_2 nanosheets, defect-rich MoS_2 nanosheets, thicker MoS_2 nanosheet assemblies, calcined MoS_2 nanosheets, bulk MoS_2, blank glassy carbon, and Pt [44], **d** STEM images of Mo and S_2 terminated edges created by the oxygen plasma in MoS_2 with 120° angle. **e** The LSV curves of MoS_2 before and after treated by oxygen plasma. **f** TEM images of the exposed edges and step-edges of the MoS_2 layers. **g** Polarization curves of MoS_2 with hydrogen annealing at various temperatures [45]

facilitate hydrogen adsorption. The ΔG_H can be dominated by strains induced by S vacancies, and thereby improving the HER kinetics. The synergistic effects of S vacancies and strains lead to an optimal $\Delta G_H = 0$ eV and attain significantly enhanced intrinsic HER activity. Thus, constructing defects for 2D nanomaterial-based electrocatalysts has been an important strategy for accelerating catalytic activity. However, controllable tuning of defects is necessary for the in-depth understanding of defects and the effects on reaction mechanisms. For example, Yao's group engineered defect-abundant graphene via removing the doped N [51]. They found that the promoted catalytic performance is strongly correlated with the defect contents induced by the removal of nitrogen, and the lower the nitrogen content, the higher the catalytic performance, further indicating that defect-engineering strategy is feasible to achieve high catalytic activity for graphene-based catalysts.

Interface engineering

Interface engineering is an essential strategy to constructing highly active catalysts with well-defined heterointerfaces. Engineering hetero-interface employing different components can modulate the surface/interface properties and electronic structures of 2D nanomaterial-based electrocatalysts, inducing novel physicochemical properties and synergistic effects, which are beneficial to the enhancement of electrocatalytic activities [23, 52]. Our group reported $Ni(OH)_2$/MoS_2 heterostructures with $Ni(OH)_2$ nanoclusters decorated on MoS_2 nanosheets for improved alkaline HER performance (Fig. 3a–c) [53]. The $Ni(OH)_2$ nanoclusters can not only improve the water adsorption/dissociation process, but also tune the electronic structures of MoS_2, thereby synergistically enhancing alkaline HER kinetics. After that, our group further proposed to decorate the basal planes of molybdenum dichalcogenides with SnS_2 quantum dots for alkaline HER (Fig. 3d) [54]. The optimal $MoSe_2$/SnS_2 heterostructured catalyst delivers significantly enhanced alkaline HER activity over pure $MoSe_2$ in 1-M KOH (Fig. 3e). The alkaline HER activity enhancement is mainly ascribed to the accelerated rate-determining water adsorption/dissociation kinetics. Meanwhile, the DFT calculations revealed that SnS_2 highly boosts the water adsorption capability of $MoSe_2$ nanosheets, which is critical for the following water dissociation process (Fig. 3f). Similarly, MoS_2/$MoSe_2$ heterostructures with MoS_2 nanoclusters anchored on $MoSe_2$ nanosheets for enhanced alkaline HER were also studied by our group [55]. MoS_2 nanoclusters were anchored on the $MoSe_2$ nanosheets, leading to more additional edge active sites (Fig. 3g–h). The optimal MoS_2/$MoSe_2$ heterostructured electrocatalyst delivers a substantially accelerated catalytic activity in 1-M KOH as compared with the bare $MoSe_2$ and MoS_2 nanosheets (Fig. 3i).

Apart from 2D TMD-based heterostructures, metal-free 2D materials can be also employed to construct heterostructures. Qiao's group coupled g-C_3N_4 with N-doped graphene (C_3N_4@NG) as a heterostructured catalyst for enhanced HER kinetics [25]. Combining the experimental findings and the DFT calculations, they found that the promoted HER activities originate from the synergistic effects of heterostructures. The g-C_3N_4 contributes to the hydrogen adsorption and N-doped graphene enhances the electron-transfer ability (Fig. 4a,b). Later, they fabricated N-doped graphene nanosheets with porous C_3N_4 nanolayers as the free-standing HER electrocatalyst [56]. The heterostructured electrocatalyst achieves exceptional HER performance with larger exchange current density, lower onset potential, and better durability as compared to commercial Pt/C. The outstanding HER performance originates from the synergistic effect of heterostructures, where in-plane porous C_3N_4 provides the exposed active sites and 3D conductive graphene network offers more electron channels. To sum up, the heterostructure design principles for 2D nanomaterial-based electrocatalysts are commonly based on the following several factors. Firstly, to fabricate the heterostructures, two (more) dissimilar components are required. Secondly, at least one component possesses catalytic activity. Thirdly, the different components should play a complementary role in electrocatalytic process. Finally, it would be better if the heterostructured catalysts are highly conductive for fast electron transfer.

Besides, atomically dispersing metal atoms on the 2D substrates are also recognized as a promising pathway to regulating the catalytic activity, because the well-defined atomic interface between single metal sites and 2D platforms can achieve the precise modulation of the local coordination environment and electronic structures, which are closely correlated with the catalytic kinetics [57]. For example, Qi et al. reported single cobalt atoms bonded to the distorted 1T MoS_2 nanosheets (SA Co-D 1T MoS_2) as an efficient HER electrocatalyst, delivering high activity and long-term stability [58]. During the synthesis process of the SA Co-D 1T MoS_2 catalyst, the formation of Co–S bond and lattice mismatch at the interface between MoS_2 and Co generate strains, which could induce the phase transition from 2H MoS_2 to distorted 1T phase. DFT calculations demonstrate that the extraordinary HER activity is attributed to the ensemble effect at the interface between the Co single atoms and the D-1T MoS_2 substrates, which can optimize the hydrogen binding energy. Zhang et al. prepared single atom Pt on the MXene support for the enhanced HER activity [59]. The modified $Mo_2TiC_2T_x$ nanosheets with abundant Mo vacancies provide large amount of anchoring sites for immobilizing Pt active centers to form Pt–C and Pt–O atomic interfaces. The developed catalyst shows an outstanding HER activity and high durability. DFT calculations

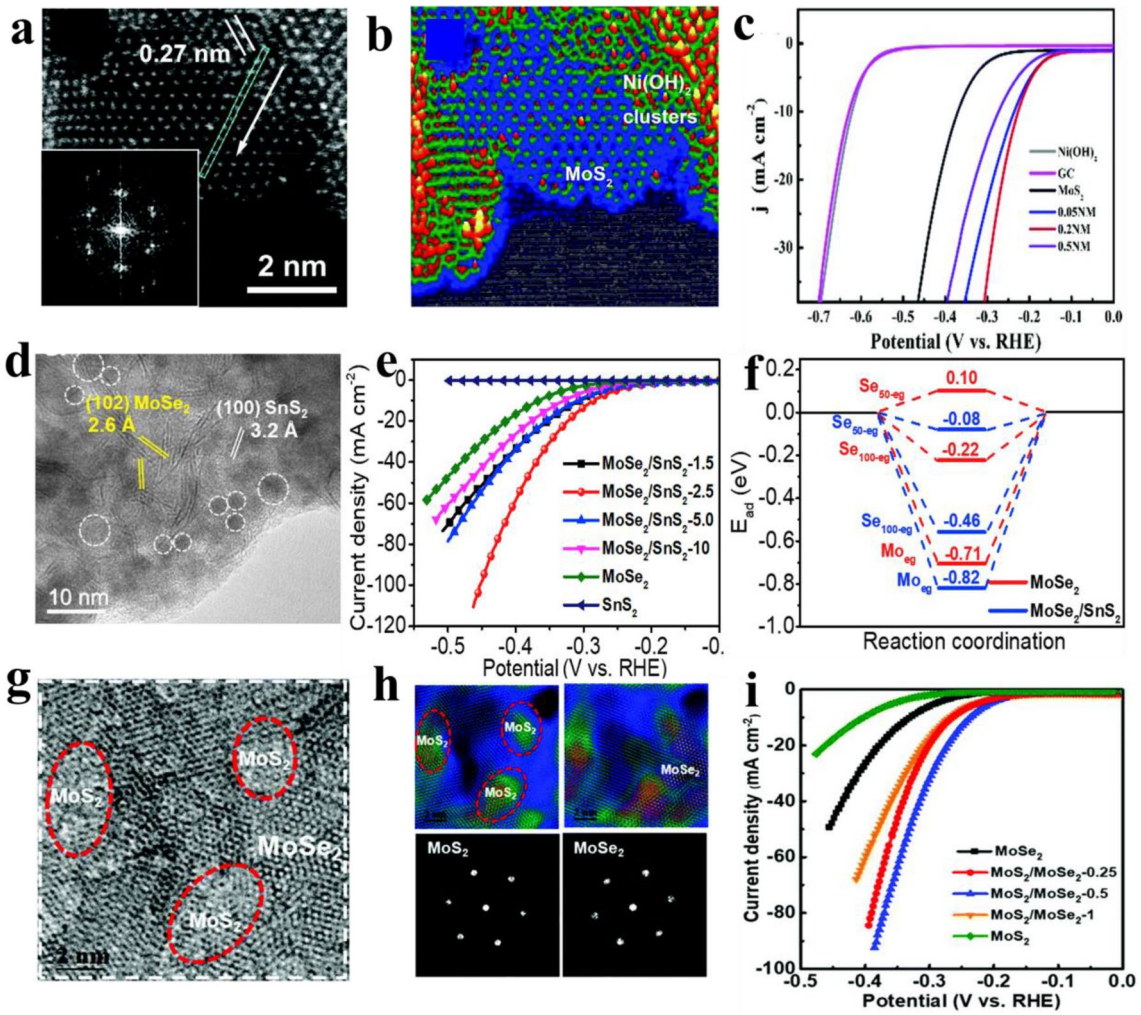

Fig. 3 **a** HAADF-STEM image of $Ni(OH)_2/MoS_2$ heterostructures. Insets: the corresponding FFT patterns. **b** The surface plot image of (**a**). **c** LSV curves of the $Ni(OH)_2$, MoS_2, and 0.05NM, 0.2 NM, and 0.5 NM (NM: the abbreviation of $Ni(OH)_2/MoS_2$ heterostructure) [49], **d** TEM images of $MoSe_2/SnS_2$-2.5 heterostructure. **e** Polarization curves of $MoSe_2/SnS_2$ heterostructures, SnS_2, and $MoSe_2$. **f** Water adsorption energy diagram for $MoSe_2/SnS_2$ heterostructures and pure $MoSe_2$ [50], **g** HRTEM image of $MoS_2/MoSe_2$ heterostructure. **h** IFFT image from the selected masked FFT patterns (top) and the selected FFT patterns (down) for $MoSe_2$ and MoS_2. **i** LSV curves of $MoS_2/MoSe_2$ heterostructures, MoS_2, and $MoSe_2$ in 1-M KOH solution [51]

reveal that the $Mo_2TiC_2O_2$–Pt_{SA} shows higher electronic energy levels and enhanced ability of electron donor than bare $Mo_2TiC_2O_2$, and achieves an optimal hydrogen adsorption free energy. Cheng et al. synthesized single Pt atoms dispersed on aniline-stacked graphene (Pt SASs/AG) via a microwave reduction method for the enhanced HER kinetics (Fig. 4c) [60]. The Pt SASs/AG catalyst delivers an outstanding catalytic performance with overpotential of 12 mV at 10 mA cm^{-2} (Fig. 4d). Also, the mass activity is 46 times higher than that of commercial 20 wt % Pt/C. Besides, the Pt SASs/AG sample achieves a remarkable stability as compared with Pt/C. X-ray absorption fine structure (XAFS) and DFT calculations demonstrate that the coordination of the N atoms originating from aniline can effectively modulate the electronic structures of Pt atoms and optimize the hydrogen adsorption energy, thereby boosting the HER kinetics. Apart from noble-metal single atoms, a number of transition-metal single atoms (e.g., Co and Ni) anchored on the functionalized graphene supports as HER electrocatalysts were also reported, and delivered promising catalytic performance [61, 62].

Phase engineering

Phase engineering for TMDs (from the semiconducting 2H phase to the metastable metallic 1T phase) can alter the bandgaps and enhance electronic conductivity. Generally, the strategies for phase engineering include alkali metal intercalation [63, 64], hydrothermal method [65], heterostructure construction [66], etc. Chhowalla's group utilized

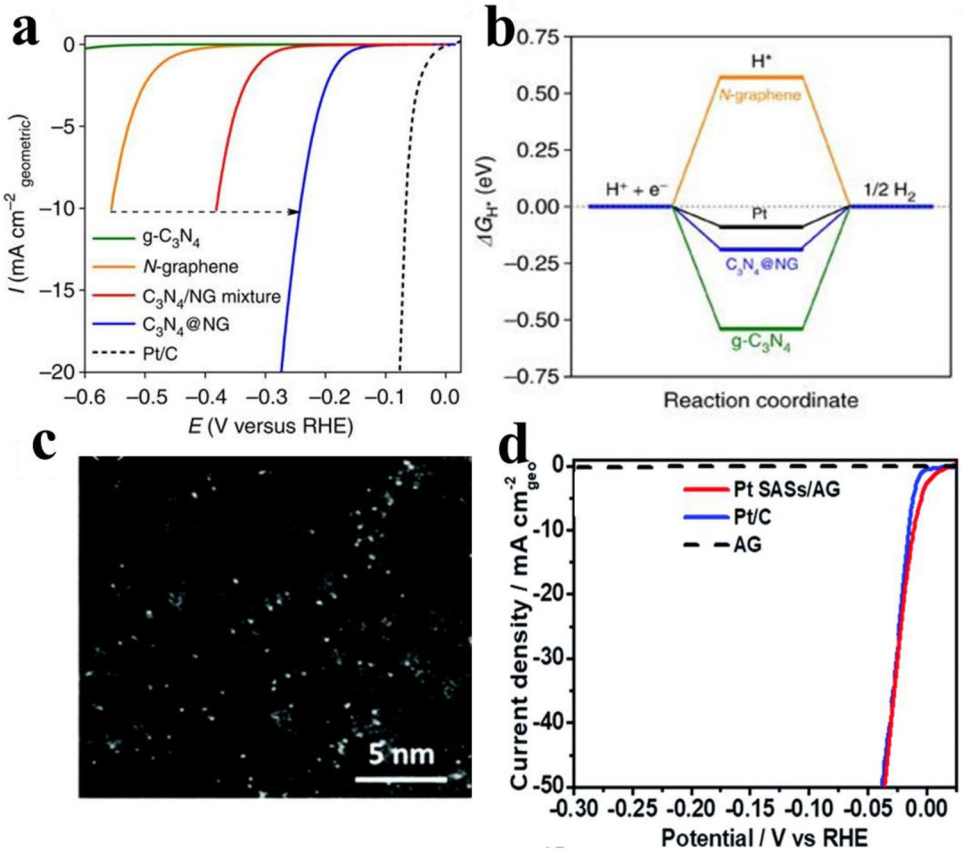

Fig. 4 **a** The polarization plots for g-C_3N_4, N-graphene, C_3N_4/NG mixture, C_3N_4@NG, and 20% Pt/C in 0.5 M H_2SO_4 at the scan rate of 5 mV s^{-1}. **b** The free-energy diagram calculated at the equilibrium potential for N-graphene, C_3N_4/NG mixture, C_3N_4@NG, and Pt [25], **c** HAADF-STEM images of Pt SASs/AG. **d** LSV curves of Pt SASs/AG and Pt/C in 0.5-M H_2SO_4 at the scan rate of 2 mV s^{-1} [56]

the solvent-free intercalation method to obtain the exfoliated MoS_2 nanosheets with a large amount of metallic 1T phases as the highly active HER electrocatalysts [63]. The MoS_2 nanosheets of 1T phase deliver superior HER kinetics after the removal of surface excess negative charges. Moreover, the HER performance of 2H phase can be significantly promoted by adding the conductive SWNTs, indicating that the poor conductivity of 2H phase is unfavorable to the catalytic activity. The results further demonstrate that 1T phase shows a better electron-transfer property than 2H phase, which is an important factor for the enhancement of the HER performance [63]. Similarly, their group exfoliated WS_2 nanosheets with a large amount of metallic 1T phase via lithium intercalation way as an efficient HER electrocatalysts [67]. The HADDF images confirm the presence of the zigzag structure in metallic 1T phase, which can induce bond strain, greatly improving the HER kinetics (Fig. 5a). Besides, the exfoliated 1T WS_2 shows excellent durability (Fig. 5b). DFT calculations further demonstrate that tensile strain is beneficial to enhance catalytic activity for WS_2 nanosheets. Therefore, the phase transition of TMDs from semiconductor 2H phase to metallic 1T phase via chemical exfoliation is an efficient way for the promotion of HER catalytic activity. Besides, Jin's group prepared partially crystallized 1T-$MoSe_2$ nanosheets composed of crystalline and disordered phase via a hydrothermal strategy [68]. They claimed that the 1T phase can effectively enhance the intrinsic activity and conductivity of the electrocatalysts; while, the disordered phase can offer plentiful defective sites as the active centers. This synergistic effect results in superior activity with overpotential of 152 mV at 10 mA cm^{-2} (Fig. 5c). 1T phase of TMDs is very unstable and tends to convert into thermodynamically stable 2H phase. Electron injection from additional components would be an efficient way to stabilize 1T TMDs phase. Zhang et al. reported 1T-$MoSe_2$/NiSe heterostructures with 1T-$MoSe_2$ nanosheets anchored on metallic NiSe nanowires [66]. The NiSe nanowires could inject electrons into $MoSe_2$ nanosheets, leading to the transition of $MoSe_2$ from 2H phase to 1T phase (Fig. 5d–f). Benefitting from the phase transition, the hybrid electrocatalysts display excellent HER activity and decent durability. This strategy can be also applied to designing other 1T MX_2-based heterostructures for various application fields.

Geometric engineering

The geometric configurations of 2D electrocatalysts significantly affect the catalytic performance due to the following reasons [69]: (1) decreasing the lateral size of 2D

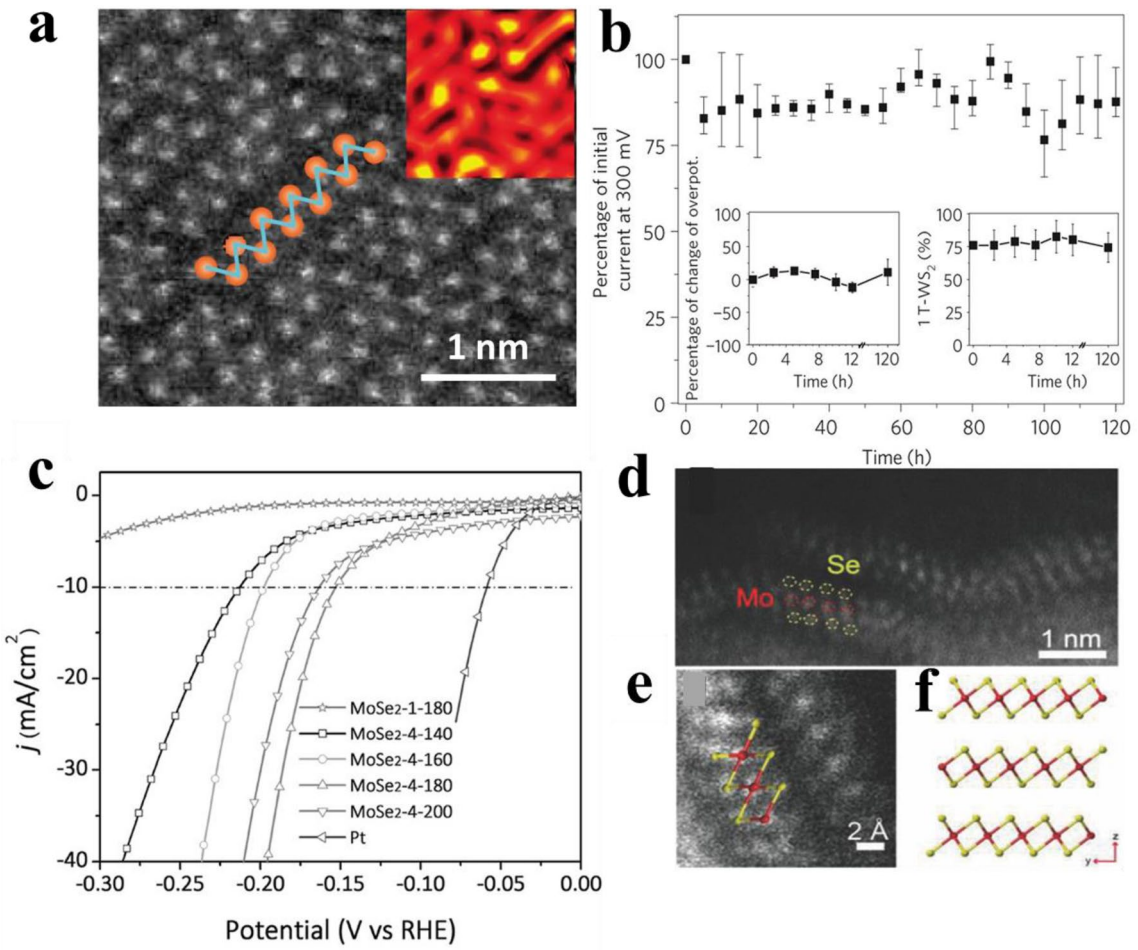

Fig. 5 **a** STEM image for the exfoliated WS_2 monolayer showing 1T superlattice. **b** The variation in current density as a function of time for 1T WS_2 electrode. The insets: the percentage of change in overpotential (left) and variation in 1T phase concentration versus time (right) [63], **c** Polarization curves of various $MoSe_2$ and Pt samples [64], **d**, **e** $MoSe_2$ nanosheet shell showing 1T-phase structure, **f** Crystal structure model of 1T-$MoSe_2$ [62]

electrocatalysts could expose more active sites [70]; (2) altering the thickness of 2D nanomaterials could modulate the electronic properties [71]; (3) reducing the thickness of 2D nanomaterials to the atomic scale is beneficial to generating more in-plane defects as additional active sites, and optimizing the electrical conductivity [72]; Li et al. reported that the ultrasmall MoS_2 particles with enrichment of S edges delivered better HER activity than the bulk counterpart [73]. Chhowalla's group discovered that reducing the thickness of WS_2 to monolayer can not only increase the exposed active sites but also induce the lattice distortions, which lead to abundant defects for hydrogen evolution [67]. Cao's group found that the HER activity of MoS_2 could be decreased by a factor of ~ 4.47 with increasing one additional atomic layer [74]. In comparison with the traditional views, they argued that increasing the atomic layer would hinder the hopping of electrons in the vertical direction of MoS_2 layers.

Conclusions and outlook

In this review, we summarized the design strategies of 2D nanomaterial-based HER electrocatalysts, including heteroatom doping, defect engineering, interface engineering, phase engineering, and geometric engineering. These strategies can efficiently optimize the electronic states, surface/interface properties, electrical conductivity, and exposed active sites of electrode materials. Even though extensive efforts have been devoted to the design of 2D nanomaterial-based electrocatalysts, it remains challenging to deliver precisely controlled synthesis, determination of real active sites, understanding of the relevant mechanisms, and cost-effective commercial applications.

First, one of the greatest challenges is how to precisely control the surface and interface chemistry in 2D nanomaterials-based electrocatalysts at atomic scale with

desired composition, defect structure and concentration, facet orientation, coordination structure, and so forth. Second, ex situ characterizations are generally applied in the investigation of the electrocatalysts and electrocatalytic reactions. The structure evolution and surface chemistry of the electrocatalysts during the electrocatalytic reactions cannot be well illustrated, which are also the typical issues in the electrocatalysis field. Furthermore, it is still very challenging to monitor the adsorption/desorption behaviors of the reaction intermediates, and, hence, one cannot capture a clear picture of the reaction processes and reaction mechanisms as well. Thus, advanced in situ/operando characterization techniques and protocols should be extensively developed to disclose the underlined structure–property relationship of the electrocatalysts and the relevant mechanisms. Third, in addition to the typical 2D TMD-based and the graphene-based electrocatalysts, some other types of 2D nanomaterials also have great potential for the development of advanced heterostructured/hybrid HER electrocatalysts, especially alkaline HER electrocatalysts. 2D-layered metal hydroxides like $Ni(OH)_2$ and $Co(OH)_2$ can serve as multifunctional substrates for constructing heterostructured alkaline HER electrocatalysts. They could not only serve as the supports for active species but also work as the co-catalysts for accelerating the rate-determining step of alkaline HER. With regard to alkaline HER, in-depth understanding of the reaction mechanism remains to be the research frontier. The g-C_3N_4 and h-BN nanosheets, which are highly stable and contain large amount of N, are also promising functional substrates for engineering heterostructured electrocatalysts. However, they are semiconductor or insulator, and possess insufficient electrical conductivity and low electrocatalytic activity. 2D metal carbides/nitrides possess high intrinsic activity [75, 76], but the lack of facile synthesis techniques would hamper their applications. Therefore, substantial efforts should be made to develop proper strategies to make full use of the advantages of these 2D nanomaterials towards the development of efficient HER electrocatalysts. Finally, there is a long way to go for 2D nanomaterial-based electrocatalysts towards practical applications. To date, there is lack of detailed performance evaluation in prototype water electrolyzers based on polymer electrolyte membranes. And, the electrocatalyst production is still at lab scale, and intensive research on large-scale production processes is urgently required.

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